ALLOTROPES OF TELLURIUM BY X-RAY DIFFRACTION METHOD*

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Plate IV

ABSTRACT. The structure of tellurium prepared by different methods was analysed by X-ray. The precipitated tellurium was so long known to be amorphous but X-ray examination revealed that it is nothing but the hexagonal variety only in a finely divided state. The diffraction patterns of tellurium were taken at different temperatures and the results obtained therein go against the hypothesis of the existence of two dynamic allotropes in ordinary tellurium. These experiments agree with the view put forward by Damiens who based his conclusions upon his own works on tellurium by chemical methods.

On chilling molten tellurium, it falls to fine powder but even this sample is not amorphous.

It was generally believed that a beam of X-rays changes the crystal structure of ordinary tellurium affecting its specific heat by about 8%, but no such change in the structure could be detected by our experiments. The diffraction pattern of liquefied tellurium was also photographed.

INTRODUCTION

Tellurium is placed in the Periodic Table along with sulphur and selenium in the 6th Group. But unlike sulphur and selenium the allotropism of tellurium is much less marked. Tellurium is known to exist in two forms—one is crystalline (hexagonal) and the other is amorphous.

Amorphous tellurium is a brownish black powder usually obtained by precipitation method, *viz.*, by reducing a solution of tellurium dioxide with sulphurous acid. It is transformed into the crystalline variety on heating with an evolution of heat.

$$Te = Te \text{ cryst.} + 2630 \text{ Cal.}$$

The density of the amorphous form ranges from 5.86 to 5.87. The specific heat is 0.052.

Molten tellurium solidifies to a brittle silvery crystalline mass, which can be easily powdered ; when obtained in appreciable size, the crystals are prismatic of the trigonal system and are isomorphous with metallic selenium.

The density of crystalline tellurium is curiously variable and depends upon the method of preparation. According to Cohen and Kromer, the density also

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changes under the influence of heat ; and this is attributed to the presence of two dynamical allotropes in ordinary tellurium ; the density as well as other properties depends on their relative proportions. This view is however contradicted by Damiens who contends that it is the impurities which cause all these inconsistencies, the correct value is 6.310.

Like density, specific heat is also variable and it ranges between 0.0475 for the distilled element to 0.6624 for the precipitated amorphous element, X-ray exposure is said to increase the specific heat by 8 p.c.

Tellurium may also be obtained in the colloidal state by a number of methods. Dilute solutions of tellurium dioxide or telluric acid on reduction, say, by hydrazine sulphurous acid etc. yield colloidal tellurium. It can also be produced by cathodic pulverisation of tellurium under water.

EXPERIMENTAL ARRANGEMENTS

As only identification rather than structure analysis was all that was necessary in the present work, only the powder method was resorted to throughout the experiment. The X-ray tube was used directly in series with the high-tension transformer without any further rectifying device. Copper K-radiation was used all along the experiment. The tube was run at 35-40 K.V. with 4-6 m.a.

The widely divergent X-ray beam coming out of the windows covered by aluminium foil of thickness 00.01 c.m. before impinging on the material became almost parallel by its passage, through a slit system.

Two types of plate-holders—cylindrical and rectangular—were used in the present work. But due to the several obvious disadvantages of the rectangular camera over the cylindrical one the preference was always given to the latter type whenever possible. Provision was made for changing the sample during the exposure without in any way disturbing the setting. For work at temperatures other than that of the laboratory, the plate camera was used with slight modifications. In the high-temperature camera, the sample was heated electrically and the double-walled film-holder is cooled by passing a cold stream of water. There was also an arrangement in which the pattern of the sample could be taken at low temperature.

The powdered material was pressed against a thin zig-zag paper which could be gummed to the slit cap with little secotine. Though the optimum thickness of the material is known to be given by $t = \frac{1}{\mu}$ (μ = mass-absorption coefficient) but trial and experiences are more reliable in this respect. Above 150°C when paper begins to char, the cells were prepared in an extremely thin walled glass tube ; capillareis were filled with the powdered mass and placed in position with both ends sealed in a groove in the cap made for this purpose. Blank exposures

were given with empty glass tube for a period longer than that necessary for powder photographs but no sign of glass band could be detected. The cell to plate distance " r " could be obtained from a reference plate of sodium chloride, photographed at the same distance.

X-Ray Examination :—According to Groth, tellurium crystallises in the hexagonal prism. It is trigonal being isomorphous with metallic selenium. The angle between the rhombohedral axis $\alpha = 56° 47'$, which corresponds with an axis ratio $a:c = 1:1.33$.

The structure of metallic tellurium was first determined by A. J. Bradley. It may be regarded as simple rhombohedral structures, with inter-axial angles of almost 90°, in which each atom is slightly displaced towards two of the six adjacent atoms. The resulting structure is a threefold spiral composed of three interpenetrating simple triangular lattices

$a = 4.445$ (A) for Tellurium.

The diffraction photographs of metallic tellurium was taken in a hemi-cylindrical camera (of radius 2.88 c.m.) with a 0.4 mm. slit. A large number of sharp rings was obtained (plate I).

These rings agree within experimental results with those calculated for hexagonal teilurium. The experiment was repeated in different camera-plate and hemi-cylindrical with different samples of tellurium and the same results was obtained (Table I).

TABLE I

Metallic Tellurium				Precipitated Tellurium		
" d " in A.U.	Sin θ	Intensity		Intensity	Sin θ	" d " in A.U.
3.67	0.2099	W	1	W	0.2068	3.72
3.05	0.2521	V.S.	2	V.S.	0.2507	3.07
2.86	0.2689	V.V.W.	3	V.V.W.		
2.24	0.3437	S	4	S	0.3407	2.22
2.12	0.3630	W	5	W	0.3592	2.14
1.99	0.3878	V.V.W.	6	V.V.W.	0.3846	2.00
1.87	0.4115	V.V.W.	7	V.V.W.	0.4131	1.86
1.76	0.4368	V.V.W.	8	V.V.W.	0.4300	1.79
			9	V.V.W.	0.4517	1.70
1.55	0.4968	V.V.W.	10	V.V.W.	0.4990	1.54
1.41	0.5461	V.V.W.	11	V.V.W.	0.5396	1.43

Precipitated tellurium (so-called amorphous variety):—Precipitated tellurium was prepared by passing slow stream of SO_2 through a solution of tellurous acid

in water at the room temperature. Tellurium so obtained in finely divided state is supposed to be amorphous. A cell of the precipitated tellurium was prepared on a zig-zag paper and exposed to X-rays for a diffraction pattern in a hemi-cylindrical camera. The cell was changed every half an hour to avoid crystallisation during exposure. The pattern, that was obtained, was obviously that due to metallic tellurium (Plate IV). The spacings calculated from measurements of the diameters are given in Table I.

The same experiment was next carried out at lower temperatures—the preparation as well as the exposure was carried nearly at 0°C by using ice as the cooling (agent) substance.

But the sample was used throughout the exposure, as there was no arrangement for changing sample in this camera. But even then the pattern consisted of rings corresponding only to metallic tellurium.

TABLE II

Specimen	Rings	Intensities	Sin θ	d in A U.
Te at room temperature	1	W	0.2085	3.69
r=4.2 c.m.	2	S	0.2498	3.08
Te at 120° C	1	W	0.2059	3.74
r=4.2 c.m.	2	S	0.2496	3.08
Te at 150° C	1	W	0.2014	3.82
r=4.2 c.m.	2	S	0.2496	3.08
Te at 160° C	1	W	0.2014	3.82
r=4.2 c.m.	2	S	0.2493	3.08
Te obtained on chilling molten Te and cooled during exposure	1	W	0.2461	3.08
r=1.94 c.m.	2	W	0.3409	2.26
Liquified Te at about 470°C	one band		0.2476	3.11
r=2.15 c.m.				

High temperature :—To test the hypothesis of two allotropes of tellurium in dynamical equilibrium, diffraction pattern of tellurium was photographed at temperatures 120°C, 150°C and 160°C. The cell used in the experiment was prepared on a zig-zag paper. Though the paper chars above 150°C, the sample together with the charred paper sticks to the cap, if undisturbed, and can be used

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 1. Pattern due to ordinary hexagonal variety of Tellurium.

Fig. 2. Pattern of precipitated Tellurium.

Fig. 3. Liquefied Tellurium.

Fig. 4. Chilled Tellurium.

at temperatures higher than this. The high-temperature camera was used and the film kept cooled throughout the exposure by passing a stream of water through the jacket. The cell was heated by passing current through a calibrated heater fitted on the cap. The results are given in Table II. No change either in intensity distribution or in the number of rings could be detected.

With a view to investigating the effect of X-ray on the crystal structure of tellurium, a diffraction photograph of tellurium was taken with cells changed every half an hour. The pattern so obtained could be compared with another due to a sample which has been exposed to X-rays for almost 24 hours. The two patterns were completely identical.

Vitreous tellurium :—In accordance with the general method of preparing vitreous substance, *viz.*, method of sudden chilling, we tried to prepare tellurium in the vitreous state by pouring molten tellurium into cold water. Tellurium so treated falls to fine powder which, on X-ray analysis, shows itself to be purely hexagonal crystal.

The experiment was next repeated in the following way—

Molten tellurium was heated nearly to its boiling temperature and then suddenly poured into a freezing mixture. The diffraction pattern of the substance thus obtained in the finely divided state was next photographed in our low-temperature camera and the sample was kept cooled near about o°C throughout the exposure. The pattern was almost identical with that of hexagonal tellurium and was different from the latter in the following two respects :

1. The number of rings present was fewer in this case, the weaker ones are found to be absent.
2. The background scattering is more pronounced than before.

DISCUSSION OF THE RESULTS

It was so long supposed that the precipitated tellurium (*i.e.*, the variety obtained by the method of precipitation) is amorphous. But X-ray examination has revealed its true identity ; it is crystalline and has the same structure as the metallic variety.

In order to explain certain anomalies in the properties of tellurium, the possibility of two allotropes, in temperature equilibrium, is proposed by some authors. If now a sample of tellurium be heated to a higher temperature the relative proportions of the two allotropes must change, which is sure to tell on the diffraction pattern of the sample. Hence it is natural to expect that at higher temperature either fresh rings will appear in the diffraction pattern of tellurium or at least the intensity distribution will change certain rings growing weaker while others grow stronger.

Now that no such change is noticeable in the pattern at higher temperatures we are forced to the conclusion that the hypothesis is untenable. The cause of above anomalies should be searched somewhere else, *viz.*, presence of impurities, etc.

X-ray exposure is said to increase the specific heat of tellurium by about 8 p.c. This increment is attributed to a change of the crystal structure, which the substance was supposed to undergo on X-ray exposure. But the pattern obtained with cells changed every half an hour showed no difference from that due to a sample exposed for 24 hours. Therefore either X-ray has very little effect on the crystal structure of tellurium or it must have produced an instantaneous effect, the crystal structure changing completely within a very short time.

Tellurium could not be prepared in the vitreous state. In this respect it differs from sulphur and selenium. Molten selenium on sudden cooling easily passes into the vitreous state. Similar method, tried in the case of tellurium, proves a failure. According to Randall a strong directive force must be present if the vitreous state is to be obtained on chilling : "In case of selenium when the crystal melts, first the spirals will break away from each other. The complete breakdown of the spiral, if it occurs at all, will take place at a higher temperature. Now in the reverse process of rapid solidification of molten selenium the atoms of a solid body always tends to arrange themselves in such positions that the crystal potential energy is a minimum for the prevailing conditions. Since in case of selenium the main energy terms lie as it were in the spirals themselves, these will try to grow immediately on solidification. It is not nearly so important for the chains to line up in full lattice arrangement. By the time the chains have grown a little the substance is too viscous to allow of any further marshalling. It is suggested therefore that strongly directional forces are necessary for the formation of glasses."*

Thus although metallic tellurium has the same crystal structure as metallic selenium, it lacks in a strong directive force while in the latter such force is present. This is to be made responsible for the difference in behaviour of tellurium and selenium as regards their production of vitreous state.

In the pattern due to chilled tellurium certain rings are absent. This cannot be attributed to any change in the crystalline nature of the substance, since it is found that it is only the weak rings which are absent. This must be due to under exposure and greater general blackening. The continuity of the rings as well as greater general blackening suggests that the operation of chilling molten tellurium must have caused a decrease in particle size of the sample. This in reality amounts to the assumption that the particle size of the chilled mass is a decreasing function of the rate of cooling, the greater the rate the smaller being the size of the individual particle.

In short, we find that tellurium whatever be its source or method of preparation is always crystalline and hexagonal in structure. The variety which had been known as amorphous is but metallic tellurium in finely divided state. It does not pass into the vitreous state on sudden cooling like selenium.

* Quoted from "Diffraction of X-rays, etc.," by Randall, p. 183.

Although the method of cooling diminishes the particle size, the crystals are not still small enough to yield bands. The more metallic character of tellurium is probably responsible for this high stability of ordinary hexagonal variety and the absence of vitreous state.

Amorphous and a new variety of tellurium :

We have seen that the process above referred to is not capable of causing diminution in particle size to the extent necessary for the production of a diffraction band. This, however, could be effected in the process of preparing a colloidal tellurium sol. where the existence of particles of the order 10^{-7} to 10^{-5} c.m. is possible.

By precipitating a colloidal solution by an electrolyte a sample of tellurium was obtained which yielded a band on X-ray exposure which corresponds in position to a strong group of rings in the hexagonal pattern. It suggests, therefore. that by this method the particle size can be made smaller than is obtainable by other methods. This will be more dilated upon in connection with colloidal tellurium solution. It is also found that certain results obtained suggest the existence of another variety of tellurium, details of which will be published in a separate paper.

LIQUID TELLURIUM

In general the diffraction pattern produced by X-rays passing through liquid is a complicated result of the structure of the actual molecules and the temporary arrangement of the molecules. Various theories have been put forward but none of them have been in any sense complete. This is but what can be expected since so little is known about the structural aspects of the liquid state.

For a practical working model, however, Stewart's ideas of cybotaxis is preferable. The following is an extract from Stewart's article in *Rev. Mod. Phys.* (2, 116, 1938) :

" If X-rays give evidence of periodic molecular grouping, it must not be supposed that these groups are large or that the molecules in any one well-defined group remain permanently members of the group. At any instant these small groups might exist at numerous points in the liquid, the regions between them being not so orderly."

Stewart argues that it is quite unlikely that catastrophic changes in atomic and molecular arrangements take place just at the melting point. Stewart's cybotactic hypothesis suggests that the kinetic energy of the molecules (in the liquid state) is of the same order as that of the binding forces among the molecules in that state.

The experimental results suggest that in a liquid there is a general tendency towards arrangements similar to those in a solid state just below the melting point. The exceptions, for which this similarity between the two states (*i.e.*, solid and liquid) do not hold, are oxygen, nitrogen and bismuth. The case of

alkali metals, lead, aluminium, appear to lie between the two extremes, while mercury fits in with the close-packing theory.

Tellurium was examined in the liquid state to test Stewart's ideas.

EXPERIMENTAL ARRANGEMENTS

Tellurium melts at 450° C, so the high-temperature camera was utilised for the investigations of the band patterns of liquid tellurium. The cell was prepared in capillary glass tube, drawn from very thin Jena glass tube. The heating could be effected by an electric heater just fitting the cap to the slit system. The heater is, in reality, a syndanio bobin wound round with nichrome wire. The heating current was produced by a step-down transformer from which steady current as high as 20 amperes could be drawn at 30 volts. The heater was calibrated so that the temperature within 2°C could be known from the current in the heating coil.

With these arrangements, exposure was given for a period of 20 hours. The pattern consisted of a single diffuse band (Plate IV). The spacings corresponding to the most intense position of the band is 3.11 (A.U.).

DISCUSSION

The value of "*d*" corresponding to the band obtained for amorphous tellurium is 3.09 (A.U.) Thus it is seen that the two "*d*" values, for liquid and amorphous are nearly equal. The slightly greater value of the former may be due to temperature effect. For hexagonal tellurium there is an intense ring of spacing 2.94 (A.U.). Thus it may be summarised that liquid tellurium also shows a similarity to the solid state.

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